Stability of Arsenic Species in Urine

Arsenic is a toxic element and a known carcinogen whose emission in the environment is strictly regulated by the US Environmental Protection Agency (EPA). The toxicity of arsenic is not only a function of the total amount of the element present, but more importantly a function of the chemical forms of the various arsenic species present. Consequently, it is critical to know the mass fraction of each arsenic species. The Centers for Disease Control and Prevention (CDC) has established a network of laboratories to monitor arsenic poisoning throughout the US by measuring arsenic species in urine. To ensure accuracy of these measurements, CDC is collaborating with NIST to develop a new Standard Reference Material (SRM) to be certified for arsenic species in frozen urine.

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NIST has established guidelines for the production and preservation of a first-of-its-kind SRM, arsenic species in urine, that call for the removal of oxygen from the urine, packaging the reference material in sealed, gas-impermeable storage containers with an oxygen absorber, and storage below freezing temperature to stabilize the material.

NIST researchers have completed a feasibility study on the production and certification of a new arsenic species in frozen urine SRM. In the course of this study, the mass fractions of the two most important species, As^{+3} and As^{+5}, were found to change as a function of time in ambient environment. A detailed study showed that As^{+3} was oxidized to As^{+5} by the oxygen in ambient air, resulting in a net decrease of As^{+3} and a net increase of As^{+5} in the specimen over time. The thermodynamics of the oxidation were investigated in search of a way to stabilize the arsenic species since the stability of analytes is critical to the viability of the reference material. It was discovered that arsenic species can be stabilized in an anaerobic environment at sub-freezing temperatures.

The results of the stability study are relevant not only to the production of a reference material, but also for routine clinical measurements where sample collection and storage prior to sample analyses can affect the accuracy of the results.

The arsenic species in urine SRM will be the first of its kind. Because the matrix of the reference material will be natural rather than processed (e.g., freeze dried), the product will be better suited for the intended purpose to validate the accuracy of methods of urine analysis. The reference material will also be the first to contain As^{+3} and As^{+5} species that are the most toxic and, therefore, more important for assessment of arsenic poisoning.

Table 1. ***Toxicity of As Species***

As Species	LD_{50} (mg/kg)	Animal
As^{+3}	4.5	rat
As^{+5}	14-18	rat
Monomethylarsonate (MMA)	1,800	mouse
Dimethylarsinate (DMA)	1,200	mouse
Trimethylarsine oxide (TMAO)	10,600	mouse
Arsenobetaine (AsB)	10,000	mouse
Arsenocholine (AsC)	6,000	mouse

LD_{50}-mass fraction at which 50 % of a population dies.

Future Plans: The guidelines developed will provide a framework for the production SRM 2669 Arsenic Species in Frozen Urine. Additional effort will be required to monitor the stability of the arsenic species over the long term to ensure the accuracy of the reference material. We will also collaborate with colleagues at CDC to improve the current procedure of specimen collection and storage prior to analysis in order to improve the accuracy of the arsenic exposure measurements.